Classical and quantum centrifugal decoupling approximations for HCl–Ar*

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The centrifugal decoupling approximation previously employed in quantum mechanics is extended to classical mechanics. Both classical and quantum centrifugal decoupling (CCD and CD, respectively) calculations are performed for HCl–Ar. Total cross sections are obtained from the CCD and CD calculations. The CCD and CD total cross sections are shown to be in good agreement with the corresponding exact classical trajectory (EC) and close coupled (CC) cross sections, respectively. The conservation of the projection (Ω) of the rotational angular momentum along the body-fixed z-axis is studied as a possible explanation for the success of the CCD and CD approximations in predicting total cross sections. By examining the CC body-fixed S-matrix elements and studying the behavior of Ω during the course of an exact classical trajectory, it is found that Ω is conserved *only* under very limited conditions. Detailed examination of the calculations shows that the CD approximation may be good even when Ω varies rapidly.

I. INTRODUCTION

One major difficulty in the theoretical treatment of molecular scattering problems lies in the large number of quantum states necessary to describe even the collision of an atom and a rigid diatom. This is a consequence of the multiplicity of projection states associated with each rotational state. In recent years this problem has led to the development of a variety of effective Hamiltonian methods.[1] By approximating the angular momentum coupling in some fashion, these methods obtain a reduction in the dimensionality of the coupled equations and thereby lead to practical computational savings in scattering problems. None of these methods has yet been fully tested as to the realm of its applicability. One of the methods which has received more attention is the centrifugal decoupling (CD) approximation (alternately termed "j_z-conserving" or "coupled states" by McGuire and Kouri).[2,3] This approach is further examined in this article. The major aim of this study was a physical analysis of certain aspects of the CD approximation.

In the CD method the coupled equations are formulated in terms of body-fixed (BF) coordinates where a computationally convenient approximation is made. The CD approximation is computationally desirable because of the resulting simplicity of the coupled equations. However, obtaining a thorough physical justification of the approximation has been a difficult task. In the CD approximation good results have been obtained for degeneracy-averaged total cross sections[3,4] with some exceptions.[5,6] In the present paper CD calculations for rotationally inelastic HCl–Ar are compared with close coupled (CC) computations. Particular attention is given to the S-matrix elements and their properties relevant to the success of this approximation.

In addition to the quantum treatments, analogous classical effective Hamiltonian calculations are performed. In classical mechanics, if action-angle variables are used,[7] the classical BF Hamiltonian has terms readily identifiable with quantum terms.[8] A precisely analogous approximation to the quantum CD approximation can be made.[9,10] The classical centrifugal decoupling (CCD) approximation is compared with exact classical (EC) trajectory calculations. The EC trajectories are examined in detail in order to gain some physical insight into the CD approximation.

It will be shown through the analysis of the exact quantum and classical results that the projection (Ω) of the rotational angular momentum along the BF z-axis can undergo large changes during an inelastic collision. This is contrary to the assumption that the coupling between different Ω values is insignificant. However, this is completely consistent with recent formulations of the CD approximation,[11] which aim to put the theory on a sounder footing. In these newer treatments off-diagonal character in Ω, which the exact calculations in this paper indicate is present, can be explicitly introduced and calculated.

II. QUANTUM INELASTIC CROSS SECTIONS

A. Computational details and theory

The computational details for the quantum centrifugal decoupling (CD) calculations are presented in this section. Included is a short summary of the necessary equations, derivation of which can be found in the literature.[1,3,12] In body-fixed (BF) coordinates and within the CD approximation, the set of coupled radial equations for an atom colliding with a rigid diatom becomes

$$\left\{\frac{d^2}{dR^2}-\frac{l(l+1)}{R^2}+k_{j'}^2\right\} U_{j'\Omega'}^{lJ\Omega}(R) = \frac{2\mu}{\hbar^2}\sum_{j''}\langle j'\Omega'|V(R)|j''\Omega'\rangle U_{j''\Omega'}^{lJ\Omega}(R), \quad (1)$$

where R is the distance between the atom and diatom,

TABLE I. Quantum total inelastic cross sections (Å^2): Centrifugal decoupling (CD) and close-coupled (CC).

	0.030 eV		0.018 eV		0.010 eV		0.005 eV	
$j \rightarrow j'$	CC	CD	CC	CD	CC	CD	CC	CD
0 1	42.7	42.5	...	45.9	42.4	41.3	31.2	24.8
0 2	21.8	21.9	25.9	25.7	22.7	22.8		
0 3	3.40	2.73	1.20	0.530				
0 4	0.181	0.132						
1 2	14.8	15.5	14.5	14.1	9.60	9.43		
1 3	3.21	3.46	1.93	1.85				
1 4	0.359	0.341						
2 3	8.19	7.94	6.27	5.87				
2 4	0.747	0.881						
3 4	3.28	3.50						

μ is the reduced mass of the colliding pair, and l is the orbital angular momentum. The rotational angular momentum, its projection along the BF z-axis (i.e., along the line of centers **R**), and the associated wavevector are represented by j, Ω, and k_j, respectively. In obtaining these equations, two approximations were made to the matrix elements of the orbital angular momentum operator $\mathbf{l}^2$: (i) The terms off-diagonal in Ω, $(\mathbf{l}^2)_{\Omega\Omega'} = -\hbar^2\delta_{\Omega',\Omega\pm1}[(J\pm\Omega+1)(J\mp\Omega)]^{1/2}[(j\mp\Omega+1)\times(j\pm\Omega)]^{1/2}$ are neglected where J is the total angular momentum; (ii) The terms diagonal in Ω, $(\mathbf{l}^2)_{\Omega\Omega} = \hbar^2\{J(J+1)+j(j+1)-2\Omega^2\}$, have been replaced by $\hbar^2 l(l+1)$. The latter association with an orbital angular momentum index (rather than J, for example) is a central part of the newer formulations which are discussed in detail elsewhere.[11] Since the potential in BF coordinates is diagonal in Ω, the first approximation leads to a set of equations [Eq. (1)] decoupled in Ω. The second approximation is also of practical usefulness since the asymptotic solutions are Bessel functions of integer order.[13]

Solution of the above equations yields the BF S-matrix elements $S^l_{\mathrm{CD}}(j'\Omega|j\Omega)$. In the new interpretation these S-matrix elements are also labeled by l; to obtain S-matrix elements labeled by J, an appropriate average is performed over the S-matrix elements labeled by an l-type index. Both of these CD elements should be distinguished from those $S^J_{\mathrm{CC}}(j'\Omega'|j\Omega)$ arrived at by solving the CC equations without the above approximations. The CC body-fixed S-matrix elements are related to the usual space-fixed (SF) S-matrix elements, $S^J(j'l'|jl)$, by a unitary transformation.[6,14]

$$S^J(j'\Omega'|j\Omega) = \sum_{ll'} i^{l-l'+j'-j}\left\{\frac{[l][l']}{[J]^2}\right\}^{1/2} \times \langle l0j\Omega|J\Omega\rangle\langle l'0j'\Omega'|J\Omega'\rangle S^J(j'l'|jl), \quad (2)$$

where $\langle\cdots\cdots|\cdots\rangle$ is a Clebsch–Gordan coefficient and $[J]\equiv 2J+1$. In the CD approximation the expression for the total cross section is:

$$\sigma^{\mathrm{CD}}(j\rightarrow j') = \sum_l \sigma^l_{\mathrm{CD}}(j\rightarrow j') = \frac{\pi}{k_j^2[j]}\sum_{l\Omega}[l]\left|\delta_{jj'} - S^l_{\mathrm{CD}}(j'\Omega|j\Omega)\right|^2. \quad (3)$$

Calculations were performed for HCl–Ar (HCl rotation constant $B = 10.5909$ cm^{-1}) using a potential given by Neilson and Gordon[15] with γ being the angle between **R** and the axis of the molecule

$$V(R,\cos\gamma) = V_r(R)[1+0.35P_1(\cos\gamma)+0.65P_2(\cos\gamma)] + V_a(R)\left[1+0.30\left(\frac{R_m}{R}\right)P_1(\cos\gamma)+0.09P_2(\cos\gamma)\right],$$

where

$$V_r(R) = \epsilon\frac{6/\alpha}{1-6/\alpha}\exp\left[\alpha\left(1-\frac{R}{R_m}\right)\right]$$

$$V_a(R) = \frac{-\epsilon}{1-6/\alpha}\left(\frac{R_m}{R}\right)^6 \quad (4)$$

The constants for HCl–Ar are $\epsilon/k = 202$ °K, $R_m = 3.805$ Å, and $\alpha = 13.5$.

Using Gordon's program,[16] the quantum coupled equations were solved at four total energies: 0.030, 0.018, 0.010, 0.005 eV. The basis set included rotational quantum numbers $0 \leq j \leq 7$. Inclusion of the three closed channels ($j = 5, 6, 7$) was necessary to achieve convergence of the basis set at the highest energy. Calculations were done at all l values in the range $0 \leq l \leq 100$. At $l = 100$ all the inelastic cross sections had converged, but many of the elastic ones were far from converged.

B. Results and discussion

The total inelastic cross sections for the quantum CD approximation are presented in Table I together with the corresponding close coupled (CC) results obtained by S. Green.[17] There is good agreement between the CC and CD inelastic cross sections; the differences between the two are mostly $\lesssim 8\%$.

A further study of the CD approximation can be obtained by examination of the S-matrix elements. The SF S-matrix elements resulting from the CC calculation can be transformed by means of Eq. (2) to yield exact BF S-matrix elements. The absolute squares of the even and odd parity S-matrix elements are given in Fig. 1 for $E = 0.010$ eV and $l = 30$. The definite parity S-matrix elements are generated by linear combinations of the usual nondefinite parity S-matrix elements.

(a)

$j\Omega$ \ $j'\Omega'$	00	10	20	11	21	22
00	.305	.027	.113	.135	.127	.294
10		.144	.185	.488	.110	.047
20			.259	.170	.091	.183
11				.008	.104	.095
21					.563	.005
22						.376

(b)

$j\Omega$ \ $j'\Omega'$	11	21	22
11	.814	.041	.145
21		.861	.098
22			.757

FIG. 1. The absolute *squares* of the BF S-matrix elements from the exact (CC) results at $E=0.010$ eV and $l=30$. Part (a) is the even parity block and part (b) is the odd parity block.[12,13] Blocks of constant Ω are boldly outlined. The lower portion of the matrices can be filled in by symmetry.

The behavior in Fig. 1 is typical of other l and E values as well. Examination of all the S-matrix elements reveals that, for a given j and j', the elements off-diagonal in Ω are frequently as large as, if not larger than, those elements diagonal in Ω.[14,18] For small l ($l\sim 5$ at $E=0.010$ eV) the off-diagonal elements are small compared to diagonal ones, but many are still significant. The elements which are insignificant represent the transitions with larger changes in Ω. Note that what is termed small l depends on E so that at higher E this behavior holds for somewhat larger values of l. The conclusion is that Ω can undergo large changes and is not conserved during collisions for practically any l value.

In attempting to explain the success of the CD approximation for the total cross sections, the simplest justification is that the terms off-diagonal in Ω, which are neglected in the CD equations, are small. The preceding finding refutes this argument. There is some indication that at small l this justification is somewhat reasonable. However, the explanation is valid only in a crude fashion and only for a small number of l values compared to the number involved at any given E, so that it cannot fully justify the CD approximation. A more complex explanation is clearly needed. A similar conclusion is obtained from the study in Sec. III.B using classical mechanics.

III. CLASSICAL INELASTIC CROSS SECTIONS

A. Computational details and theory

This section presents results for classical cross sections using both exact classical (EC) trajectories and classical centrifugal decoupling (CCD) trajectories. The EC expressions are given in terms of action-angle-like space-fixed (SF) coordinates,[19] whereas the CCD expressions are given in terms of action-angle-like body-fixed (BF) coordinates.

The quantum mechanical expression for the rotational cross section of an atom colliding with a rigid diatom in the space-fixed axis system is[20]

$$\sigma(j\to j')=\frac{\pi}{(2j+1)k_j^2}\sum_{Jll'}(2J+1)\left|\delta_{jj'}\delta_{ll'}-S^J(j'l'|jl)\right|^2. \tag{5}$$

This expression can be converted into its primitive semiclassical form by performing the following: (i) introducing the primitive semiclassical form of the S-matrix,[21] (ii) converting the sums in Eq. (5) into integrals, and (iii) ignoring interference effects so that partial averaging techniques[22] may be applied. In step (ii) it is convenient to introduce the variables $\hat{j}$, $\hat{l}$, and $\hat{J}$ which are the classical analogues of j, l, and J and they are defined by $j+\frac{1}{2}$, $l+\frac{1}{2}$, and $J+\frac{1}{2}$ (note $\hat{n}\equiv n+\frac{1}{2}=[n]/2$ where the latter notation was used in Sec. II). Similarly the relative radial momentum P_R is the classical analogue of the wavevector k_j. All these variables are in units of $\hbar=1$.

The expression which results from the procedure mentioned above is

$$\sigma(j\to j')=2\pi\int_0^\infty b\,db S(b), \tag{6}$$

where the expression for the impact parameter

$$b=\hat{l}/P_R \tag{7}$$

has been introduced. The function $S(b)$ is defined by

$$S(b)=\int_{|\hat{j}-\hat{l}|}^{\hat{j}+\hat{l}}\frac{\hat{J}}{2\hat{j}\hat{l}}\,d\hat{J}\int_0^\pi\frac{d\bar{q}_l}{\pi}P_{j';j}, \tag{8}$$

where $P_{j';j}$ is the probability for the transition $j\to j'$ for fixed $\hat{l}$, $\hat{J}$, P_R, and $\bar{q}_l$, whose semiclassical value is

$$P_{j';j}=s\sum_{\text{s.p.}}\left|\frac{\partial\hat{j}^f}{\partial\bar{q}_j 2\pi}\right|^{-1}_{\hat{j}^f=\hat{j}'}, \tag{9}$$

where s.p. denotes stationary phase and s is a symmetry factor[23] equal to unity for systems such as HCl–Ar. The sum in Eq. (9) for $s=1$ is over all values of

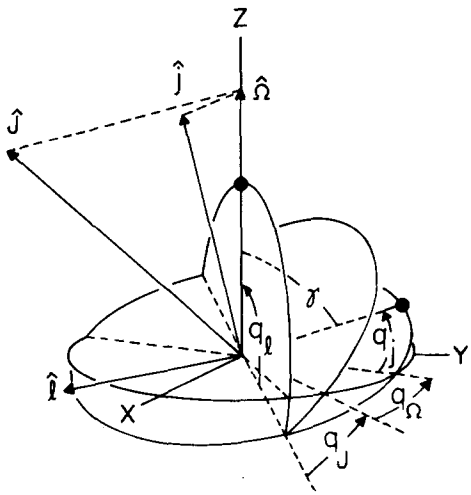

FIG. 2. Definitions of body-fixed action-angle-like variables: $\hat{j}$, $\hat{J}$, $\hat{\Omega}$, q_j, q_J, and q_Ω given with space-fixed action-angle-like variables $\hat{l}$ and q_l. The particle along the z-axis represents the incoming Ar atom while the particle in the q_j-plane represents the H atom of the rotor.

$\bar{q}_j$ in the interval $(0, 2\pi)$ which give the final value of the rotational angular momentum $\hat{j}^f = \hat{j}'$. The specially defined variables $\bar{q}_j$ and $\bar{q}_l$ are canonically conjugate to the final $\hat{j}$ and $\hat{l}$.[24] The probability in Eq. (9) can be reduced to its classical analogue by integrating the right hand side of Eq. (9) over $\hat{j}'$ in the interval $(\hat{j}' - \frac{1}{2}, \hat{j}' + \frac{1}{2})$ and partial averaging.[25] Thus the classical probability becomes

$$P_{j';j} = \int_0^{2\pi} d\bar{q}_j p(\bar{q}_j), \tag{10}$$

where (for $s = 1$) $p(\bar{q}_j)$ is unity if $\hat{j}' + \frac{1}{2} > \hat{j}^f \geq \hat{j}' - \frac{1}{2}$ and is zero otherwise. For systems such as H_2–H ($s = 4$),[23] the limits on the integral become $(0, \pi)$ instead of $(0, 2\pi)$ and $\hat{j}^f$ must satisfy $\hat{j}' + 1 > \hat{j}^f \geq \hat{j}' - 1$. Equations (6)–(8) and (10) are the desired expressions which comprise the EC cross section.

The classical cross section in BF variables can be derived in a manner analogous to that shown above starting from the appropriate quantum expression. The resulting expression is

$$\sigma(j \to j') = \frac{\pi}{k_j^2} \int_0^\infty \frac{\hat{J}}{\hat{j}} d\hat{J} \int d\hat{\Omega} \int_0^{2\pi} \frac{dq_\Omega}{2\pi} P_{j';j}, \tag{11}$$

in which P is the same as before and the limits on the integral over $\hat{\Omega}$ are $(-\hat{j}, \hat{j})$ if $\hat{j} < \hat{J}$ and $(-\hat{J}, \hat{J})$ if $\hat{j} > \hat{J}$. The projection $\hat{\Omega}$ of $\hat{j}$ (or $\hat{J}$) on the BF z-axis is given in terms of SF variables by

$$\hat{\Omega} = \frac{[-\hat{J}^4 - \hat{l}^4 - \hat{j}^4 + 2\hat{j}^2\hat{l}^2 + 2\hat{j}^2\hat{J}^2 + 2\hat{J}^2\hat{l}^2]^{1/2} \sin q_l}{2\hat{l}}, \tag{12}$$

where q_l is the SF angle conjugate to $\hat{l}$ whose asymptotic value is $\bar{q}_l$. The variable $\hat{\Omega}$ and its conjugate BF angle q_Ω are shown in Fig. 2 along with the BF angle q_j.

The CCD approximation enters the equations of motion governing the trajectories by introducing the BF effective Hamiltonian

$$H_{CCD} = \frac{P_R^2}{2\mu} + \frac{1}{2\mu R^2}[\hat{j}^2 + \hat{J}^2 - 2\hat{\Omega}^2] + B\hat{j}^2 + V(R, \cos\gamma), \tag{13}$$

where γ is the usual angle entering the intermolecular potential and may now be expressed as $\cos\gamma = (1 - \hat{\Omega}^2/\hat{j}^2)^{1/2} \sin q_j$, where q_j is the BF q_j. This effective Hamiltonian insures that $\hat{\Omega}$ is constant. The classical analogue of replacing $J(J+1) + j(j+1) - 2\Omega^2$ by $J(J+1)$ in the effective Hamiltonian affords no particular advantage in the classical computations and this approximation has not been made. Since q_Ω is absent from the potential and because $\hat{J}^2$ is generally larger than $\hat{j}^2 - 2\hat{\Omega}^2$, the neglect of this latter term should not significantly affect the results. If the CCD approximation is not made, the Hamiltonian contains an additional term of the form

$$(\sqrt{\hat{j}^2 - \hat{\Omega}^2}\sqrt{\hat{J}^2 - \hat{\Omega}^2}\cos q_\Omega)/\mu R^2 .$$

By taking matrix elements of this term using semiclassical wavefunctions in action-angle variables,[26] the quantum result for off-diagonal matrix elements $(l^2)_{\Omega\Omega'}$ is obtained. This term is then the exact classical analogue of the term omitted in the quantum Eq. (1).

For collisions in which $\hat{j}$ remains larger than zero, it is possible for $\hat{\Omega}$ to approach $\pm\hat{j}$ during the collision. When this occurs, q_Ω becomes ill-defined and BF action-angle-like coordinates may not be used. To circumvent this problem, initial conditions were specified in BF coordinates, a transformation was made to SF action-angle-like variables, the classical trajectory was performed, and a transformation was made back to BF variables. For collisions in which $\hat{j}$ approaches zero, q_j becomes ill-defined and the trajectories must be calculated in Cartesian coordinates.

Calculation of cross sections using the EC and CCD methods involves evaluating a four-dimensional integral. Stratified Monte Carlo[27] techniques were applied to this evaluation in the following way. For the EC calculation sample points were picked uniformly at random for values of $\hat{J}$ and $\bar{q}_l$ lying in their total respective ranges of integration while the integral over b was divided into strata and the sample point was picked from one of the strata. For strata which gave larger contributions to the integral, more sample points were used to more efficiently improve the accuracy of the result. Once a sample point was chosen, 24 trajectories were computed classically for equispaced values of $\bar{q}_j$ in the interval $(0, 2\pi)$. The probability was then calculated by dividing the number of points for which $\hat{j}' + \frac{1}{2} > \hat{j}^f \geq \hat{j}' - \frac{1}{2}$ by 24. For the CCD calculations, sample points were chosen uniformly at random for $\hat{\Omega}$ and q_Ω while the integral over $\hat{J}$ was stratified. Trajectories for the CCD method were computed using the effective Hamiltonian in Eq. (13) and the rest of the procedure is the same as that described above.

B. Results and discussion

Rotationally inelastic cross sections were calculated for HCl–Ar at total energies of 0.030 and 0.056 eV. In Table II the EC and CCD cross sections for $3 \to j'$ and the EC cross sections for $0 \to j'$ are given for $E = 0.030$

eV. This table also contains the corresponding CC and CD quantum results. The agreement between the EC and CC results is only good for the $0 \rightarrow 1$ and $0 \rightarrow 2$ transitions. For the other transitions the EC results are too large. Table III presents the EC and CCD cross sections for $4 \rightarrow j'$ at $E = 0.056$ eV. The ± limits on the total cross sections are reasonable estimates of the statistical error.

The agreement between the EC and CCD results in both Tables II and III is approximately as good as the agreement between the CC and CD results in Table I. As can be seen from the partial averaged semiclassical cross section expressions in Eqs. (9) and (11), the probability term for inelastic energy transfer contains only direct dependence on the bulk energy transfer. The effect of the reorientations of the rotational angular momentum vector does not directly enter Eq. (9) and is averaged over in Eq. (11) (i.e., in the same fashion that Ω and Ω' are summed over to obtain the quantum mechanical $j \rightarrow j'$ cross section). For situations such as broadening and shifting of rotational lines, however, the CD approximation could sometimes lead to inadequate results since there the reorientation effect due to collisions enters the line shape expression directly.[23] This difficulty would occur for line shapes or other problems not dominated by $j \rightarrow j'$ transitions.[28]

An interesting physical effect observed in the classical calculations was orbiting at large impact parameters ($b \sim 10$ a.u., $E = 0.030$ eV). All cases of observed orbiting were approximately rotationally elastic and should have no direct effect on the classical inelastic cross sections. The range of impact parameters where orbiting occurred was about 0.5 a.u. wide. This behavior might indicate that quantum resonance effects may be significant. This point was not explored in the quantum calculations which were only for inelastic transitions.

A careful analysis of the trajectory data at $E = 0.030$ eV was made to gain physical insight into the CD approximation. At small impact parameters ($b < 3.0$ a.u. or $l < \sim 20$) the value of $\hat{\Omega}$ was often nearly constant throughout the trajectory. However, at larger impact parameters this near conservation breaks down, and

TABLE II. Comparison of exact classical (EC), classical centrifugal decoupled (CCD), close coupled (CC) and quantum centrifugal decoupled (CD) inelastic cross sections in Å^2 for $E = 0.030$ eV.

Transition	Classical		Quantum	
$j \rightarrow j'$	EC	CCD	CC	CD
$0 \rightarrow 1$	38.1 ± 2.0	•••	42.7	42.5
$0 \rightarrow 2$	23.5 ± 1.2	•••	21.8	21.9
$0 \rightarrow 3$	7.0 ± 0.5	•••	3.40	2.23
$0 \rightarrow 4$	0.3 ± 0.1	•••	0.181	0.132
$3 \rightarrow 0$	2.0 ± 0.4	1.1 ± 0.3	1.02	0.672
$3 \rightarrow 1$	3.7 ± 0.5	4.8 ± 0.6	2.64	2.85
$3 \rightarrow 2$	13.3 ± 1.1	14.2 ± 1.2	9.08	8.81
$3 \rightarrow 4$	7.5 ± 0.5	7.5 ± 0.5	3.29	3.50

TABLE III. Comparison of the exact classical (EC) and classical centrifugal decoupled (CCD) inelastic cross sections in Å^2 for $E = 0.056$ eV.

Transition	Classical	
$j \rightarrow j'$	EC	CCD
$4 \rightarrow 0$	0.2 ± 0.1	0.1 ± 0.1
$4 \rightarrow 1$	0.6 ± 0.1	0.4 ± 0.1
$4 \rightarrow 2$	2.4 ± 0.3	2.1 ± 0.3
$4 \rightarrow 3$	9.0 ± 0.7	8.2 ± 0.7
$4 \rightarrow 5$	5.1 ± 0.4	5.5 ± 0.7
$4 \rightarrow 6$	0.06 ± 0.02	0.02 ± 0.01

at very large impact parameters ($b > 14$ a.u.) one finds $\hat{\Omega}_{\text{final}} = -\hat{\Omega}_{\text{initial}}$. A typical trajectory is illustrated in Fig. 3 for the region of impact parameters that gives large contributions to the total inelastic cross section. During the collision $\hat{j}$ changes rapidly but only at short range, while $\hat{\Omega}$ varies more slowly but continuously throughout the whole trajectory. However, most of the $\hat{\Omega}$ variation occurs within the same time period ($\sim 0.7 \times 10^5$ a.u.) of the overall $\hat{j}$ change. Examination of a large number of classical trajectories confirms the conclusion from quantum arguments (Sec. II.B) that $\hat{\Omega}$ does undergo large changes for a wide range of l values. The simplest model which assumes conservation of Ω is therefore insufficient by itself to explain the success of the CD approximation. In addition no clear separation of the $\hat{j}$ and the $\hat{\Omega}$ behavior is observed so that these results do not provide an unequivocal example of the more complex model proposed by McGuire.[29]

Finally, recall that quantum mechanically the computational reduction of the CD calculation over the CC calculation is enormous. Classically, the trajectory computation time and hence the time required to calculate the cross sections is approximately equivalent in the EC and CCD methods. An *exact* semiclassical

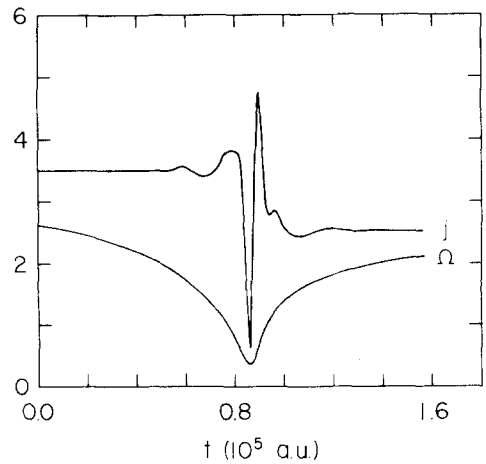

FIG. 3. The variation of $\hat{j}$ and $\hat{\Omega}$ as a function of time. $E = 0.030$ eV, $J = 44.879$. At $R = -\infty$, $\hat{j} = 3.500$, $\hat{\Omega} = 3.194$, $\overline{q}_j = 0.785$, $\overline{q}_l = 1.867$, and $l = 43.702$. At $R = +\infty$, $\hat{j} = 2.526$ and $\hat{\Omega} = 2.385$. The time $t = 0$ corresponds to $R = 20$ a.u.

(exact Hamiltonian plus classical S-matrix) calculation of the inelastic cross sections was also initially attempted. The number of stationary phase points involved in the evaluation of Eq. (9) was large (8–12) for HCl–Ar, and the number of trajectories to find all of them would have required a substantial amount of computer time. For that reason exact semiclassical HCl–Ar calculations were not performed.

IV. CONCLUSIONS

For HCl–Ar the classical centrifugal decoupling approximation has been shown to give agreement with EC total cross sections as good as that commonly obtained between the CD and CC total cross sections. While the CD approximation affords a large computational savings over CC calculations, the CCD and EC classical trajectory calculations require approximately the same amount of computer time. However, pure classical calculations in this framework exhibit their usefulness as a means for physical analysis of effective Hamiltonian approximations.

The simplest model for the CD approximation assumes that Ω is conserved. Both quantum (through S-matrix elements) and classical observations of Ω lead to the conclusion that Ω in general does change significantly for HCl–Ar. Only for small l is near conservation of Ω seen. This model was, therefore, rejected as a general explanation of the success of the CD approximation. The present paper indicates that it is necessary to explore further physical models for the CD approximation.

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